SOLUBILITY OF NATURAL GAS IN VARIOUS CRUDE OILS

and

PREPARATION OF PURE METHANE FROM NATURAL GAS

Thesis by

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INTRODUCTION

The work reported in this paper is a continuation of experiments begun and carried out by B.H.Sage, and described in his thesis for the Masters degree C.I.T. 1931. The object of the research was to determine as quantitatively as possible the solubility of natural gas in various crude oils, as it was known that by dissolving natural gas in crude oil, the physical properties of the oil could be changed in such a way as to make possible greater recovery of the crude oil from the underground formation. As pointed out by Mr. Sage, the solubility figures presented in his thesis had to be arrived at by a method of approximation as he was then not experimentally able to measure the change in liquid volume resulting from dissolved gas. In order to make possible more accurate calculation of gas solubility, apparatus was designed and installed for directly measuring the change in volume of the crude oil which occurred as a result of dissolved gas. Other changes were made in the equipment as first set up by Mr. Sage, which were designed to increase accuracy and speed in carrying out the experiments. These changes will be discussed in the main body of this report.

The solubility data presented in all cases is for a temperature of 100°F and pressures ranging from zero to 2500 lbs. per sq. in. The following representative crude oils were used: Sugarland, Texas; Yates, Texas; Ventura, Calif.; Santa Fe Springs, Calif.; Bartlesville, Okla.; Seminole, Okla.; Lima, Ohio; and Bradford, Pa. These crudes as used were saturated with air at atmospheric pressure.

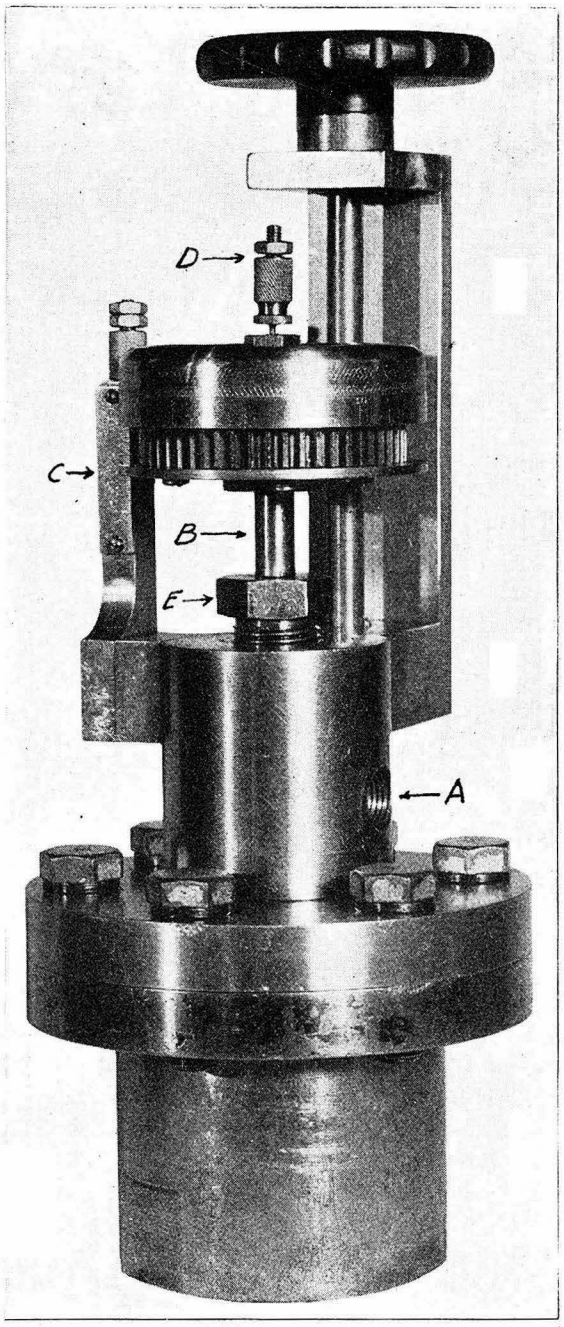
Dry Santa Fe Springs natural gas was used in all cases.

DETERMINATION OF SOLUBILITY

A definite weight of crude oil was placed in a steel cell capable of withstanding pressures up to 3000 lbs. per sq. in. The temperature of the cell was maintained practically constant, and measured quantities of gas were pumped into it. For each successive portion of gas admitted the equilibriul pressure in the cell, and the volume of the liquid phase, were recorded. The total volume of the cell, and the liquid volume being known, the free gas space over the crude oil could be determined by difference. Knowing this volume and the compressibility of the natural gas used, the quantity of gas over the oil for each equilibrium point could be calculated. By subtracting this figure from the quantity of gas admitted to the cell, the solubility value for the natural gas was determined.

METHOD OF PROCEDURE

A sample of the crude oil to be used in a solubility run was weighed in a flask, a portion of the sample was then poured into the solubility cell(Fig. 1), and the flask re-weighed. The weight of sample taken was determined by difference. In order to know the volume which a definite weight of crude oil would occupy in the cell,after it had come to temperature, the gravity of the crudes used was determined at 100°F by means of a picnometer. Knowing the weight of crude taken and the gravity at the temperature in question, the initial volume of the oil sample in the cell could be calculated. After placing the crude oil in the thick walled steel cell, the top of the cell was bolted on tight,



Solubility Cell.

Fig.1

A- Gas inlet port

B- Micrometer for measuring liquid level

C- Scale for micrometer

D- Electric contact for level indicator

E- Packing gland for shaft

and the whole assembly placed in a rocker arm in an oil bath. The gas line from the compressor was then connected by means of a standard fitting(see Thesis of B.H.Sage). The oil level in the bath was then raised by forcing in more oil, under air pressure, from a reserve tank, until the cell was just covered. The oil bath was provided with a steam coil and electric heaters. After the bath had been brought approximately to temperature the electric heaters on the mercury regulator were adjusted so as to maintain very nearly a constant temperature. Fluctuations of temperature could be held to within 0.04 of a degree Centigrade. At the same time that the oil bath was coming to temperature the electric heaters on the gas lines were turned on, and they too brought to temperature. Line temperatures were measured by means of thermocouples soldered onto the steel tubing. Both lines and mercury traps (to be discussed later) were heated to 100 °C. The cell was given time to come to thermal equilibrium, and then the liquid level in the cell was measured. This was accomplished by means of a special type of apparatus to be reported on by B.H.Sage in his thesis for the Ph. D. degree. Briefly the method was as follows: A very small wire, forming one side of a bridge circuit, was attached to one end of a micrometer screw which passed thru the top of the cell (see Fig.1). While the wire was in the gas phase a small current was passed thru it, and the bridge brought into balance as shown by a galvanometer. The micrometer screw was then lowered into the cell until a sudden deflection of the galvanometer needle, resulting from the bridge circuit becoming unbalanced, indicated that the wire

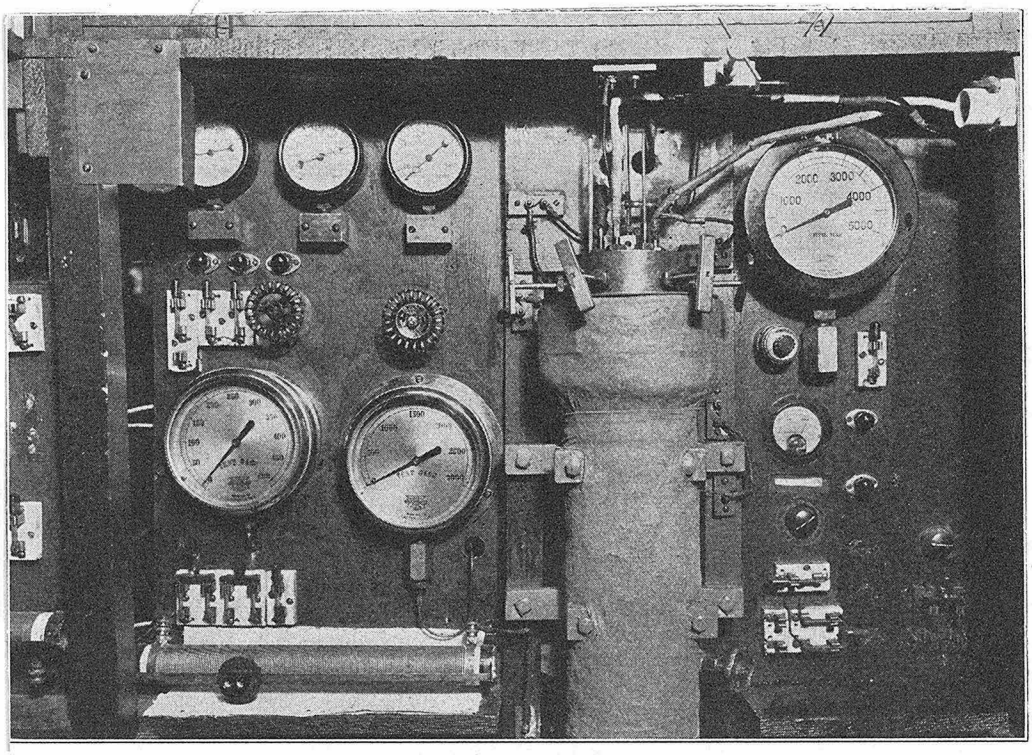
was touching the liquid. The bridge circuit was thrown out of balance because the liquid conducted heat away from the wire much faster than the gas did, there-by changing the temperature and resistance of the wire. By means of this device the liquid level could be measured to within a thousandth of an inch. The volume of the liquid as determined by measurement agreed very closely with that calculated from the weight and gravity of the crude oil.

Temperatures being correct the run could be started. In order to obtain a solubility figure the quantity of gas admitted to the cell had to be measured. This was accomplished by drawing gas out of a calibrated reservoir held at constant temperature, and observing the fall in pressure. The method was that outlined by F.P.Stapp in his thesis for the Masters degree. The reservoir consisted of a steel cell placed in a bath of diethyleneglycol, the temperature of which could be closely maintained at 100 °C. The pressure in the reservoir was determined by placing weights on a fluid pressure balance. As this type of equimpent was used throughout for measuring pressures it will be described here. The cell in which the pressure was to be measured was provided with a mercury trap similar in shape to the conventional U tube, but made of steel. Gas from the cell was in contact with one side of the mercury column while the other side was connected by means of a copper tube to the standard type of Crosby fluid pressure scale. This whole system, including line and tester, was completely filled with a light oil, giving only a fluid medium between the mercury trap and the pressure measuring instrument. Whatever pressure was applied to one side of the mercury U by the gas in the cell

was directly transmitted by means of a fluid system to the balance. The instrument was so designed that the pressure was determined by placing weights on a balance arm until the beam was brought into balance. One important condition however had to be met if the pressures read were to mean anything, and that was that the volume of the system concerned must remain constant. This was provided for by placing a pointed contact on the oil side of the mercury trap in such a way that, as the mercury level changed, a circuit including an indicating light was made or broken. Due to the compressibility of the oil, slight leaks in the fluid system, and at times a small amount of gas in the lines, some means had to be provided for adding more oil to the system in order that the mercury column could be held at just the proper place. This oil was added by means of a screw plunger,which was an integral part of the Crosby instrument, and which when screwed down forced more oil into the lines. Whenever a pressure reading was taken the oil in the line and trap was adjusted until the indicating light just went out, there-by giving a constant volume on the cell side of the trap. These mercury traps were also electrically heated and thermally regulated so as to avoid condensation of gas in the trap. Throughout the rest of this report whenever pressure measurements are reported it is to be understood that they were taken in the manner described above. Two separate balances were used; one covering the range zero to 3000 lbs. per sq. in. and capable of being read to the nearest pound, the other covering the range zero to 300 lbs. per sq. in. and capable of being read to the nearest tenth of a pound. The former was used for measuring the equilibrium pressure in the saturation cell, and the latter for measuring the pressure in

the reservoir. Valves placed in the bottom of the mercury traps permitted one side of the mercury U to be shut off from the other side. By closing this valve the gas side of the trap could be evacuated without causing any trouble in the oil side of the trap.

The gas measured out of the calibrated reservoir was taken into the gas compressor(Fig.2), which was a large steel cylinder connected by means of a throttle valve to a pump which supplied mercury under pressure. This mercury was used as a piston, increasing the pressure on the gas as more mercury was forced into the cylinder. The compressor used was the same in principle as that reported in the thesis of B.H. Sage. Instead of using high pressure air as the source of power for driving the mercury into the gas cylinder, a Worthington steam-driven plunger pump was used. By regulating the steam pressure to the pump the mercury system could be put under any desired pressure. This pump had the advantage that it could be run under practically stalled conditions, there-by avoiding heavy impact pressures on the mercury lines when the throttle valve was closed. As in the compressor previously used, this one was provided with electric light contacts in the side of the cylinder and a carbon rod in the top for indicating the position of the mercury in the compressor. The carbon rod being one side of a bridge circuit containing an indicating galvanometer the exact position of the mercury in the top of the compressor could be determined. The mercury was always brought to the same height in the small tube in the head of the cylinder, there-by maintaining a constant total volume for the solubility system. Also by this means the free gas space in the top of the cylinder, after the gas had been



Gas Compressor and Control Panel.

Fig.2

forced out of the compressor into the solubility line and cell, could be reduced to a negligible fraction of the total volume of the system. In order to avoid condensation in the compressor the mercury from the pump was heated by a steam jacket before entering the compression chamber. The cylinder itself was electrically heated and lagged with insulating material. The temperature was maintained at about 100°C by means of an electric relay and thermostat in the heating circuit. The temperature was taken by means of a thermometer placed in a well in the head of the compressor.

At the start of a run the reservoir, compressor and lines were evacuated; the cell however not being evacuated, as the composition of the oil might have been changed slightly in so doing. The reservoir was then filled with gas up to the desired pressure. As previously stated gas was withdrawn from the reservoir, and admitted to the compressor forcing the mercury present there thru a release valve into a storage bomb, which was used to supply mercury to the pump. Air pressure of about 50 lbs. per sq. in. was maintained over the mercury in this storage tank in order to force it quickly and easily into the pump. For this reason the pressure in the reservoir cell could not be dropped much below seventy pounds. When the desired amount of gas had been admitted to the compressor, the mercury release valve was closed and then the reservoir line shut off. Mercury under pressure was then admitted to this closed system compressing the gas in the cylinder as the volume became less and less. A steel tube bourdon gage on the mercury inlet line indicated roughly the pressure of the gas in the compressor. When this pressure was greater than the pressure in the solubility

cell, which was known from the scale reading, the valve to the solubility line was opened and the gas forced out until the mercury in the compressor had risen to the shut-off point, as shown by the galvanometer reading. The solubility line valve was then closed, and the motor started which rocked the cell, agitating the liquid within. This caused the pressure to fall, as gas went into solution. The agitation was continued until the pressure remained constant, as shown by the balance, at which time it was assumed that equilibrium had been reached. The time required to reach saturation was never more than five minutes. The agitation was then stopped, and the rocker arm moved until a leveling glass indicated that the cell was in a vertical position. Several minutes were allowed for drainage of the liquid on the inside cell walls, and then the liquid level was measured in the manner described above. This reading was taken several times, and could be made to duplicate very closely. The pressure reading was taken at a time when the level indicator was just in contact with the liquid. This was done in order that a small correction could be made in the total volume of the cell due to the fact that the shaft for the level indicator occupied space. From this reading and the reading taken at the beginning of the run when no gas was present, the per cent change in liquid volume could be calculated. Once the liquid volume had been determined for a particular pressure reading, and the shaft correction deducted from the total volume of the cell, the free gas space over the liquid could be calculated. After each equilibrium pressure had been determined, and the corresponding liquid level measured, more gas was admitted in the same manner as above umtil the maximum pressure

desired for the run had been reached. At the end of the run oil was removed from the bath until the cell was uncovered, and then the crude oil and gas were blown out of the cell by opening a plug in the bottom of the cell. This was done in order to avoid blowing the cell down thru the gas inlet line, as crude oil would then be carried over and deposited in that system.

DETERMINATION OF THE COMPRESSIBILITY OF NATURAL GAS USED

In order to arrive at a figure for the solubility of the natural gas in the crude oil it was necessary to determine what portion of the gas admitted to the cell was present in the free space over the oil. By subtracting this amount of gas from the total gas measured in, the amount in the oil phase could be determined. The quantity of gas required at a given temperature to bring one c.c. of free space in the cell up to a particular pressure was determined in the following way: A run similar in all respects to that carried out for a solubility determination was made, with the exception that no crude was placed in the cell. The quantity of gas admitted and the corresponding pressures were recorded. Then a second run was made similar to the first except that a steel slug of accurately known volume was placed in the cell. By plotting for each of these two runs the quantity of gas admitted to the cell against pressure in the cell the amount of gas occupying the space corresponding to the volume of the steel slug could be determined directly by difference. From this a figure could be calculated for the quantity of gas occupying a c.c. of space in the cell at a particular temperature and pressure. The total volume of the cell and the liquid volume being known for each equilibrium point of a

solubility run, the free gas space over the crude oil could be found by difference. From this, and the compressibility of the gas as determined above the total quantity of gas over the oil could be calculated. The difference between this figure and the total amount of gas admitted to the cell was the amount actually present in the crude oil phase. This method while giving a figure for gas solubility is not however entirely accurate owing to a peculiar phenomenon which takes place due to solubility of gas in the crude oil. It has been experimentally observed that some of the light hydrocarbon constituents present at the start in the crude oil, leave the oil phase and pass into the vapor phase when the crude is placed in contact with natural gas under high pressure. The reason for this phenomenon is no doubt related to the fact that fugacity changes with pressure. When this occurs the composition of the gas over the oil would be changed slightly and therefore its compressibility factor might be changed slightly. An even larger difference between the composition of the gas over the oil and the composition of the gas used for the compressibility determination results from the differential solubility of the constituents making up the natural gas. The errors thus introduced could not be evaluated, and so were not taken into account in the data as reported.

SAMPLE CALCULATION

The data used is taken from a run using dry Santa Fe Springs natural gas and Lima crude oil. The symbol "H" specifies the position of the micrometer screw used in determining the liquid level.

Weight of crude oil placed in the cell	51.02 gm.
Initial volume of crude oil	62.75 c.c.
Total volume of cell when "H" is zero	138.25 c.c.

Saturation pressure in cell 1964 lbs. per sq. in.
Total volume of gas admitted to cell 15,764 c.c. (70 °F)
Liquid volume as determined by "H" reading 74.33 c.c.
Volume correction for micrometer screw 0.33 c.c.
Volume of cell less correction 137.9 c.c.
Free gas space over liquid 137.9 - 74.3 = 63.6 c.c.
From compressibility data for a pressure of 1964 lbs. per sq. in. we find that 14,700 c.c. of gas (measured at 70 F and 1 atmosphere) occupy 87.69 c.c. of actual space in the cell.

Therefore the amount of gas in the free space over the crude oil = $\frac{14700}{87.69} \times 63.59 = 10,660$ c.c.

By difference the amount of gas in the liquid phase = 15,764 - 10,660 = 5104 c.c.

The solubility figure is then $\frac{5104}{51.02} = 100$ c.c./gm.

When experssed in terms of cu. ft. per barrel of initial crude oil this figure is 459.3

The relative volume of the liquid is $\frac{74.33}{62.75} = 1.184$

DISCUSSION OF RESULTS AND PLOTS OF DATA

In the case of a crude oil of high A.P.I. gravity (low density) part of the more volatile hydrocarbon constituents, as mentioned above, may pass from the liquid phase to the gas phase as the pressure of natural gas applied over the crude is increased. If one now assumes that in a solubility run equilibrium is attained between all of the molecular species in the gas phase and the corresponding molecular species in the liquid phase, then it becomes important to know the ratio of the total volume of the cell to the initial volume of oil taken. The greater the free gas space over the crude oil the larger the quantity of a particular volatile hydrocarbon that will

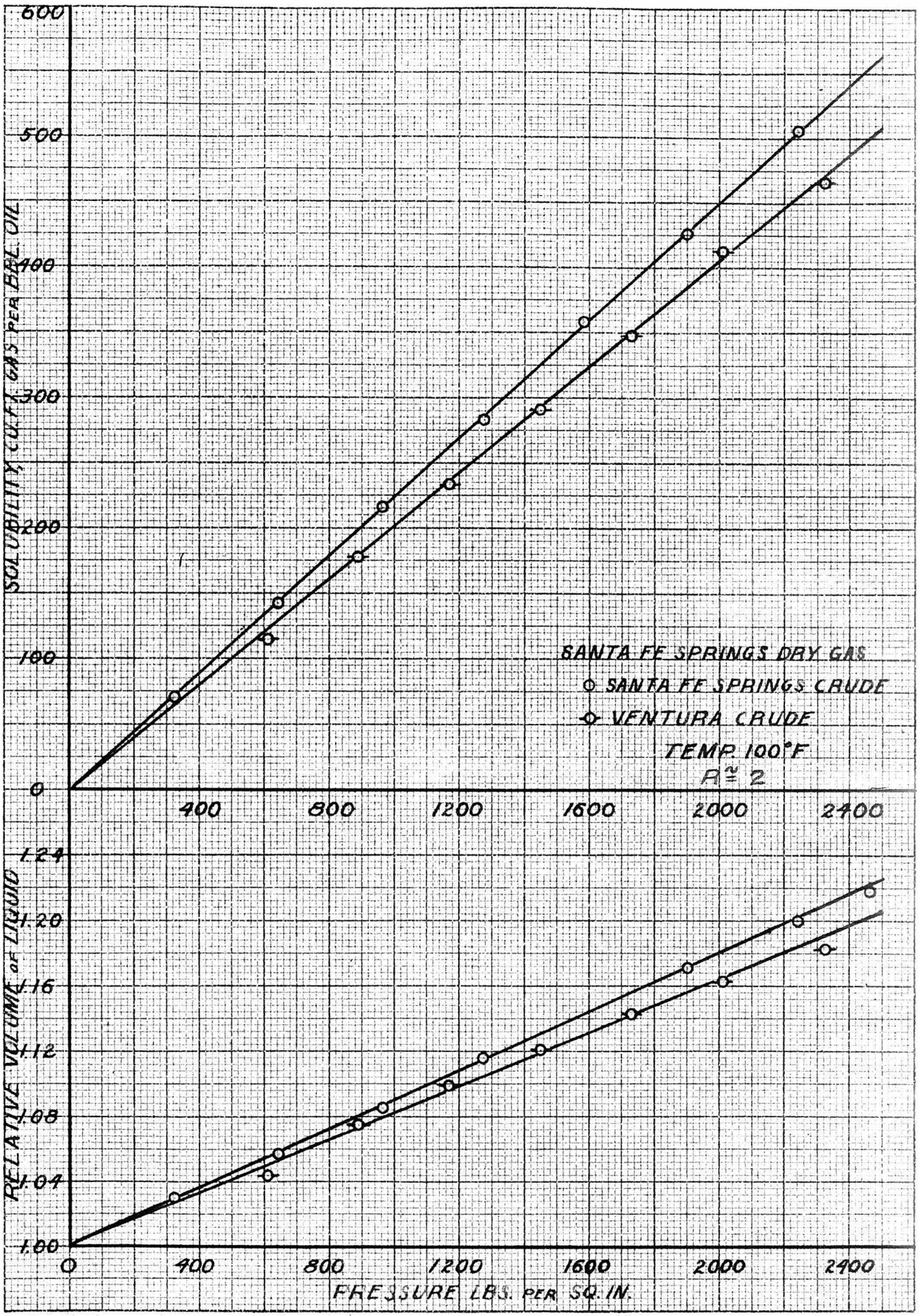
have to leave the liquid phase in order to produce the required equilibrium partial pressure in the gas phase. As an aid in specifying starting conditions, and for convenience in correlating with other data, the ratio of total cell volume to initial volume of oil taken is recorded for each run. In all cases this ratio was approximately 2.

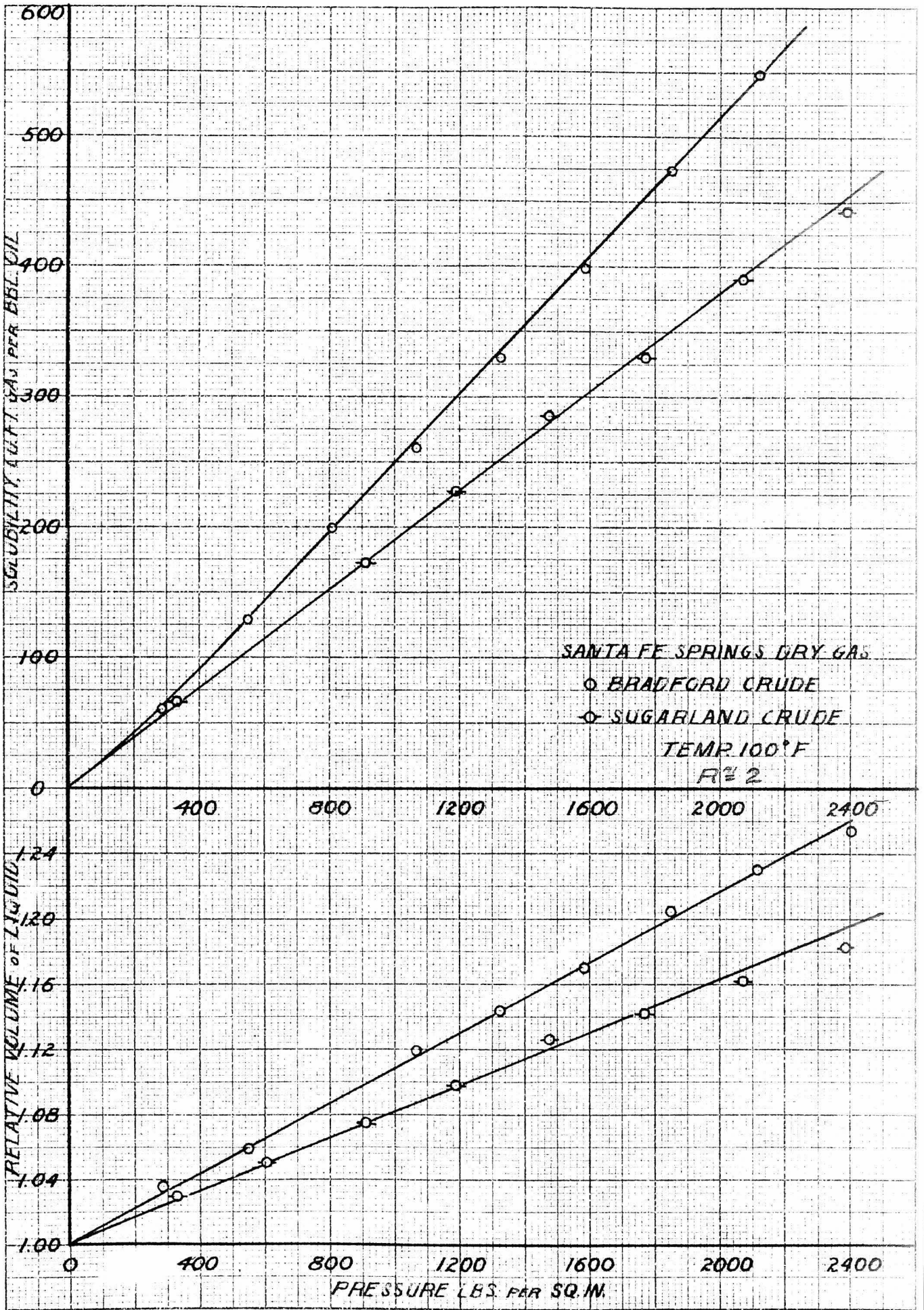
Solubility values are given in terms of cu. ft. of gas per barrel of initial crude oil. (For units see appendix). The relative volume of the liquid is the ratio of the liquid volume for the particular saturation point, to the initial volume of crude oil in the cell at the temperature of the run.

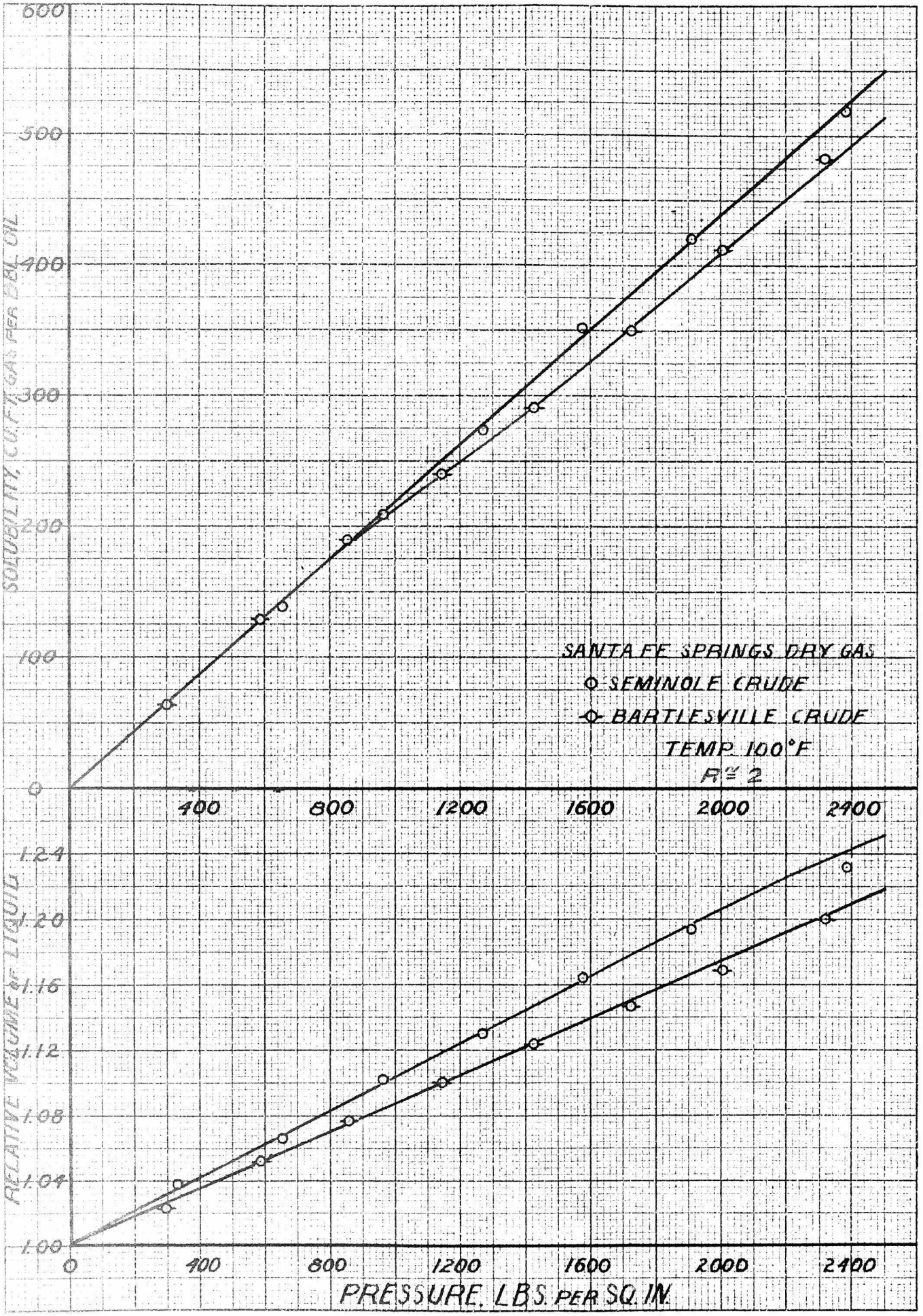
In some cases the plots of solubility and relative volume of liquid against pressure resulted in straight lines, while in others there is a definite falling off in slope at the highest pressures. Because of the complexity of the system (both the gas and the crude oil containing a number of different constituents), and the scarcity of information regarding such mixtures, it is at present almost impossible to explain the irregularities which occur in the curves. As a first approximation one might say that the solubility of natural gas in crude oil is directly proportional to pressure over the range from zero to 2500 lbs. per sq. in. An interesting result is obtained when solubility is plotted against change in volume of the crude oil. It was found that, for the rather wide variety of crudes studied, the change in volume of the liquid phase in all cases, except that of Seminole crude, was, within 10%, the same for corresponding saturation values. That is to say that for a definite quantity of gas dissolved in an equal

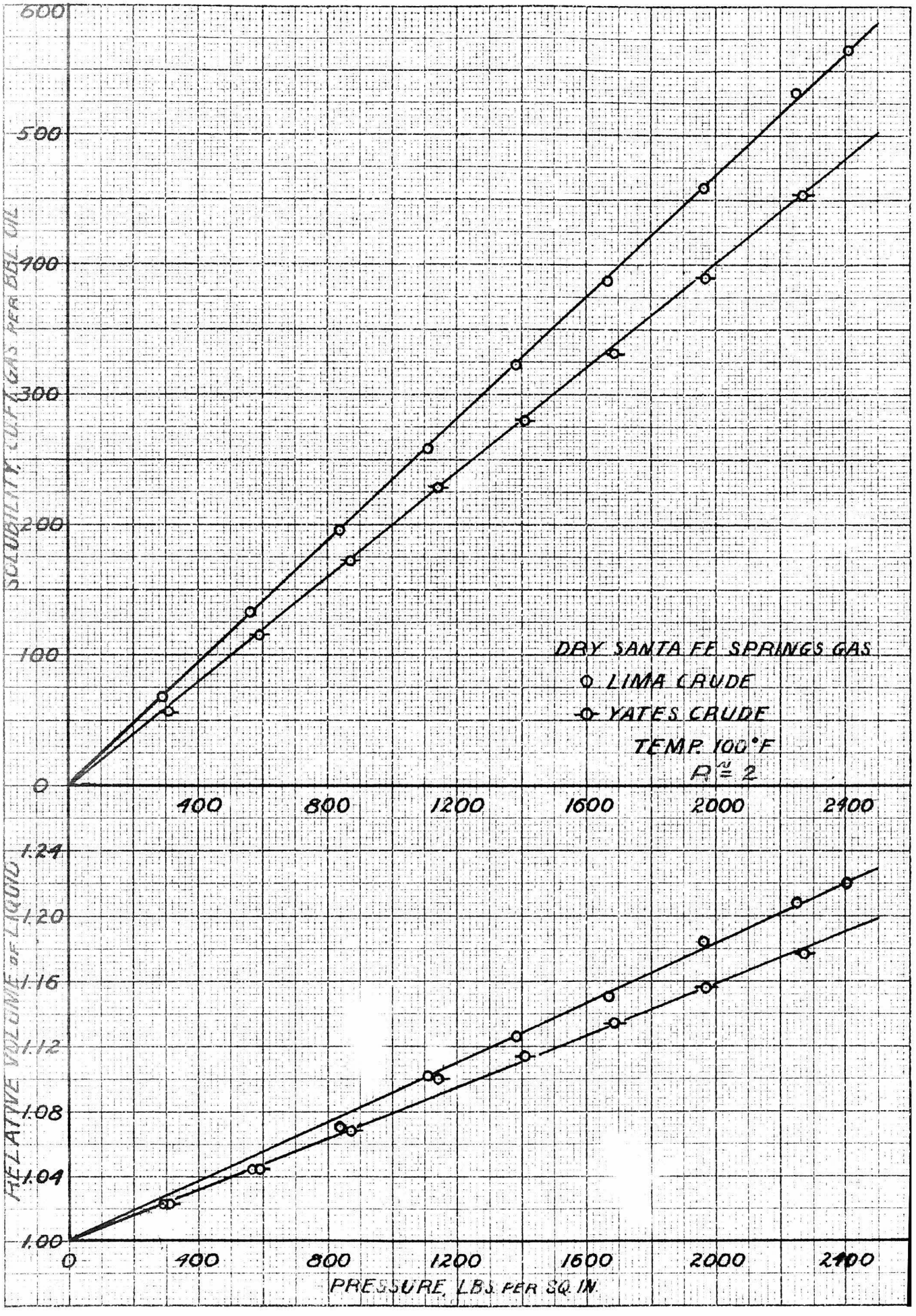
volume of any one of the above mentioned crudes, the resulting change in liquid volume would be of the same order of magnitude. Furthermore the data when plotted in this way gave practically straight lines, showing that the change in liquid volume was proportional to the quantity of dissolved gas.

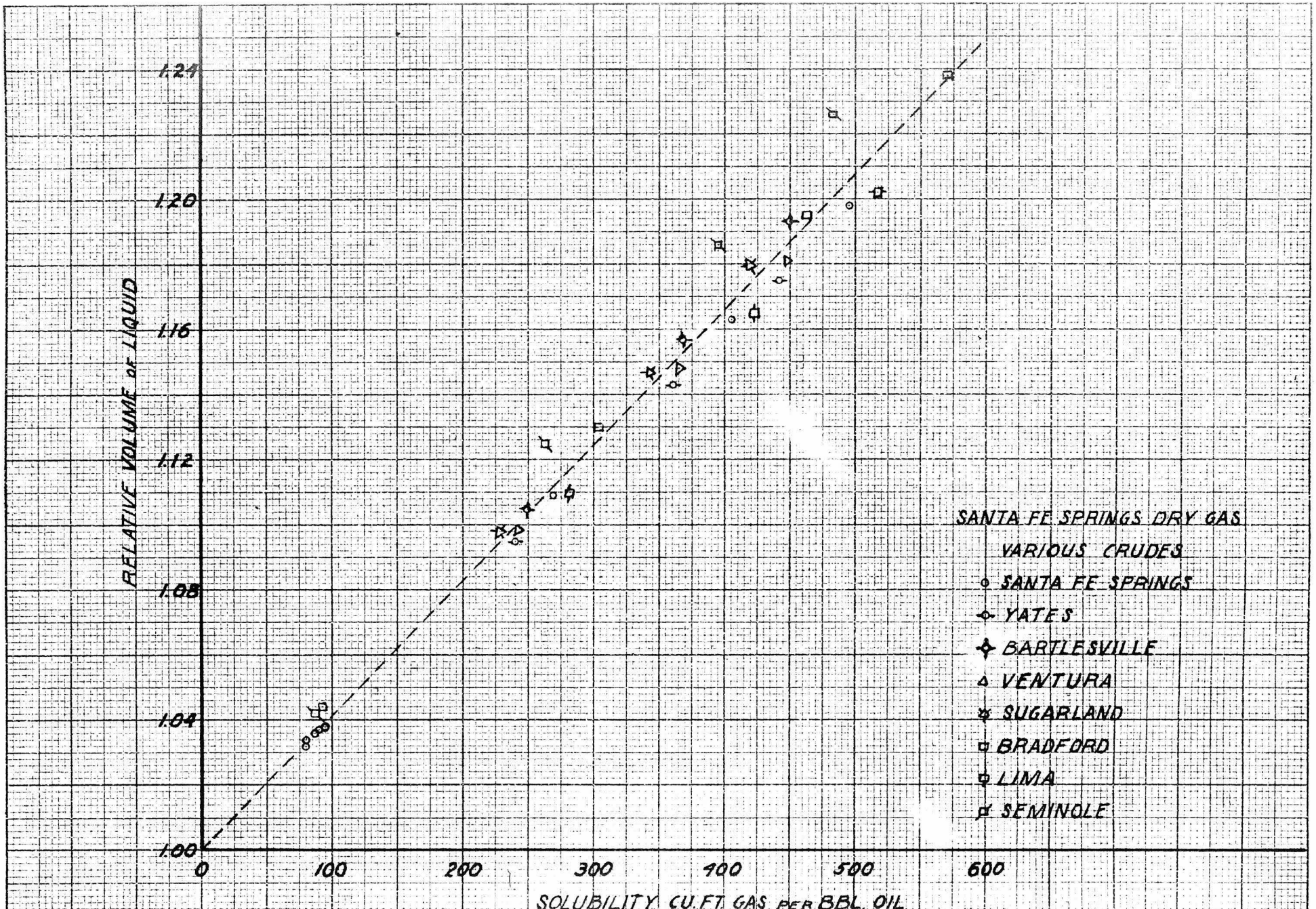
Another interesting relation is that obtained by plotting gas solubility, for a particular temperature and pressure, against the gravity of the crude oil. From this one sees that natural gas is more soluble in the lighter crude oils, that is oils with higher A.P.I. gravity. Perhaps a better relation than this could be obtained if it were possible to plot solubility against average molecular weight of the crude oil.

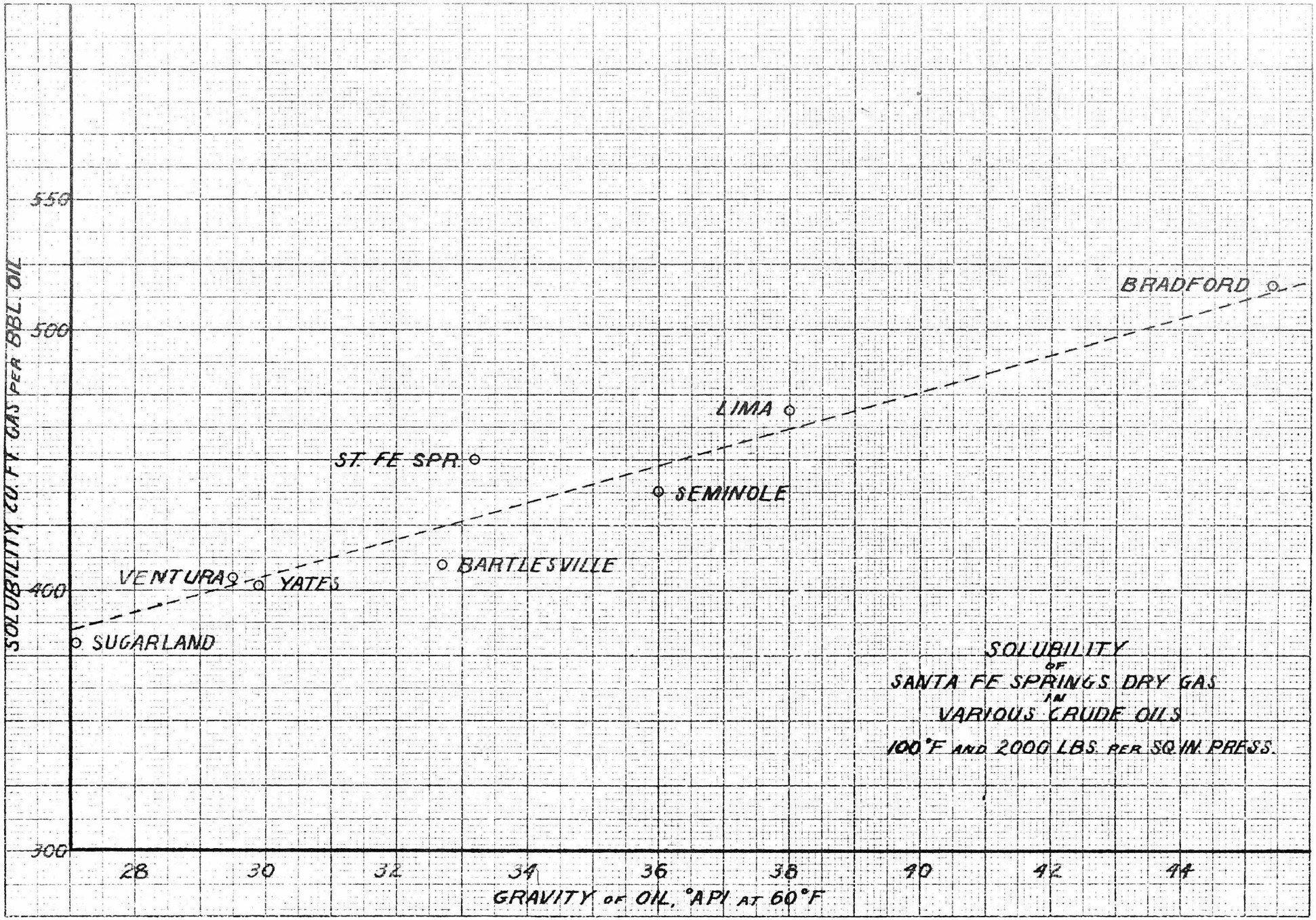

SOLUBILITY, CU. FT. GAS PER BBL. OIL
600
500
400
300
200
100
0
400
800
1200
1600
2000
2400
SANTA FE SPRINGS DRY GAS
SANTA FE SPRINGS CRUDE
VENTURA CRUDE
TEMP. 100°F
A ≅ 2
RELATIVE VOLUME OF LIQUID
1.24
1.20
1.16
1.12
1.08
1.04
1.00
0
400
800
1200
1600
2000
2400
PRESSURE LBS. PER SQ. IN.


SOLUBILITY, CU.FT. GAS PER BBL. OIL
600
500
400
300
200
100
0
400
800
1200
1600
2000
2400
SANTA FE SPRINGS DRY GAS
BRADFORD CRUDE
SUGARLAND CRUDE
TEMP. 100° F
R = 2
RELATIVE VOLUME OF LIQUID
1.24
1.20
1.16
1.12
1.08
1.04
1.00
0
400
800
1200
1600
2000
2400
PRESSURE LBS. PER SQ. IN.


SOLUBILITY, CU. FT. GAS PER BBL. OIL
600
500
400
300
200
100
0
400
800
1200
1600
2000
2400
SANTA FE SPRINGS DRY GAS
SEMINOLE CRUDE
BARTLESVILLE CRUDE
TEMP. 100°F
R = 2
RELATIVE VOLUME OF LIQUID
1.24
1.20
1.16
1.12
1.08
1.04
1.00
0
400
800
1200
1600
2000
2400
PRESSURE, LBS. PER SQ. IN.


SOLUBILITY, CU.FT. GAS PER BBL OIL
600
500
400
300
200
100
0
400
800
1200
1600
2000
2400
DRY SANTA FE SPRINGS GAS
LIMA CRUDE
YATES CRUDE
TEMP. 100°F
P = 2
RELATIVE VOLUME OF LIQUID
1.24
1.20
1.16
1.12
1.08
1.04
1.00
0
400
800
1200
1600
2000
2400
PRESSURE, LBS. PER SQ. IN.


1.24
1.20
1.16
1.12
1.08
1.04
1.00
RELATIVE VOLUME OF LIQUID
0
100
200
300
400
500
600
SOLUBILITY, CU.FT. GAS PER BBL. OIL
SANTA FE SPRINGS DRY GAS
VARIOUS CRUDES
SANTA FE SPRINGS
YATES
BARTLESVILLE
VENTURA
SUGARLAND
BRADFORD
LIMA
SEMINOLE


SOLUBILITY, CU. FT. GAS PER BBL. OIL
550
500
400
300
BRADFORD
LIMA
ST. FE SPR.
SEMINOLE
BARTLESVILLE
VENTURA
YATES
SUGARLAND
SOLUBILITY OF SANTA FE SPRINGS DRY GAS IN VARIOUS CRUDE OILS
100°F AND 2000 LBS. PER SQ. IN. PRESS.
28
30
32
34
36
38
40
42
44
GRAVITY OF OIL, °API AT 60°F

PREPARATION OF PURE METHANE FROM NATURAL GAS

INTRODUCTION

Realizing that the solubility of a natural gas in crude oil was partly a function of the composition of the gas, it was deemed advisable to make solubility runs using pure gases, with the hope that it would be possible to correlate the data for the pure and mixed gases. Methane, being the component present in largest amount in most natural gases, was obviously the first gas to begin work with. Difficulty was encountered at the very start, as it was found impossible to obtain methane of sufficient purity on the market. It was therefore necessary to design and set up laboratory apparatus capable of producing methane containing not more than 0.3% of heavier hydrocarbons. The method of procedure used was determined largely by the facts that the prepared gas was needed at a pressure of at least 300 lbs. per sq. in., and that with such pressures sufficient quantities could be stored in steel cylinders of small actual volume. From the standpoint of expense and convenience it was decided to use natural gas as the source of methane, which is usually present in amounts ranging from 75% to 85%. During the first stage of experimentation dry Santa Fe Springs natural gas was used, but later on it was found desirable and feasible to use ordinary city gas.

METHOD OF PROCEDURE

The general plan of procedure was to condense out, by means of high pressure and low temperature, practically all of the constituents in the natural gas heavier than ethane, and then to separate the methane from the ethane and remaining heavier hydrocarbons by means of selective adsorption on charcoal.

The equipment necessary was, therefore, a gas pump for producing high pressure, a low temperature condensation trap, and charcoal cells designed to operate under pressure. At first the attempt was made to use the compressor designed for the solubility work. Briefly the procedure was as follows: Dry Santa Fe Springs natural gas was pumped by means of the compressor into a steel bomb, immersed in a bath of alcohol and solid carbon dioxide, until the pressure in the bomb was about 2000 lbs. per sq. in. At this pressure and a temperature of about -70 °C most of the hydrocarbons heavier than propane would condense out. The resulting gas, consisting largely of methane and ethane, was then passed thru a charcoal cell operating under a pressure of about 800 lbs. per sq. in., and held at a temperature of about 10 °C. Here, due to selective adsorption, practically all of the ethane was removed, leaving almost pure methane, contaminated chiefly by nitrogen which was not removed by the charcoal.

This procedure did not prove satisfactory for several reasons. In the first place the compressor was not adapted for this particular type of continuous operation, and therefore the manipulations were slow and tedious. The wear and tear on the compressor valves was excessive, and furthermore the compressor could not be used for the solubility work when methane was being prepared. A change was also desirable which would make it possible to produce methane containing less oxygen and nitrogen. The method of procedure finally decided upon is set forth in the flow sheet of Fig.3. Gas was drawn from the city lines into a motor-driven single stage compressor, which delivered the gas at a pressure of about 300 lbs. per sq. in. The gas then passed thru a trap filled with cotton, where entrained oil particles

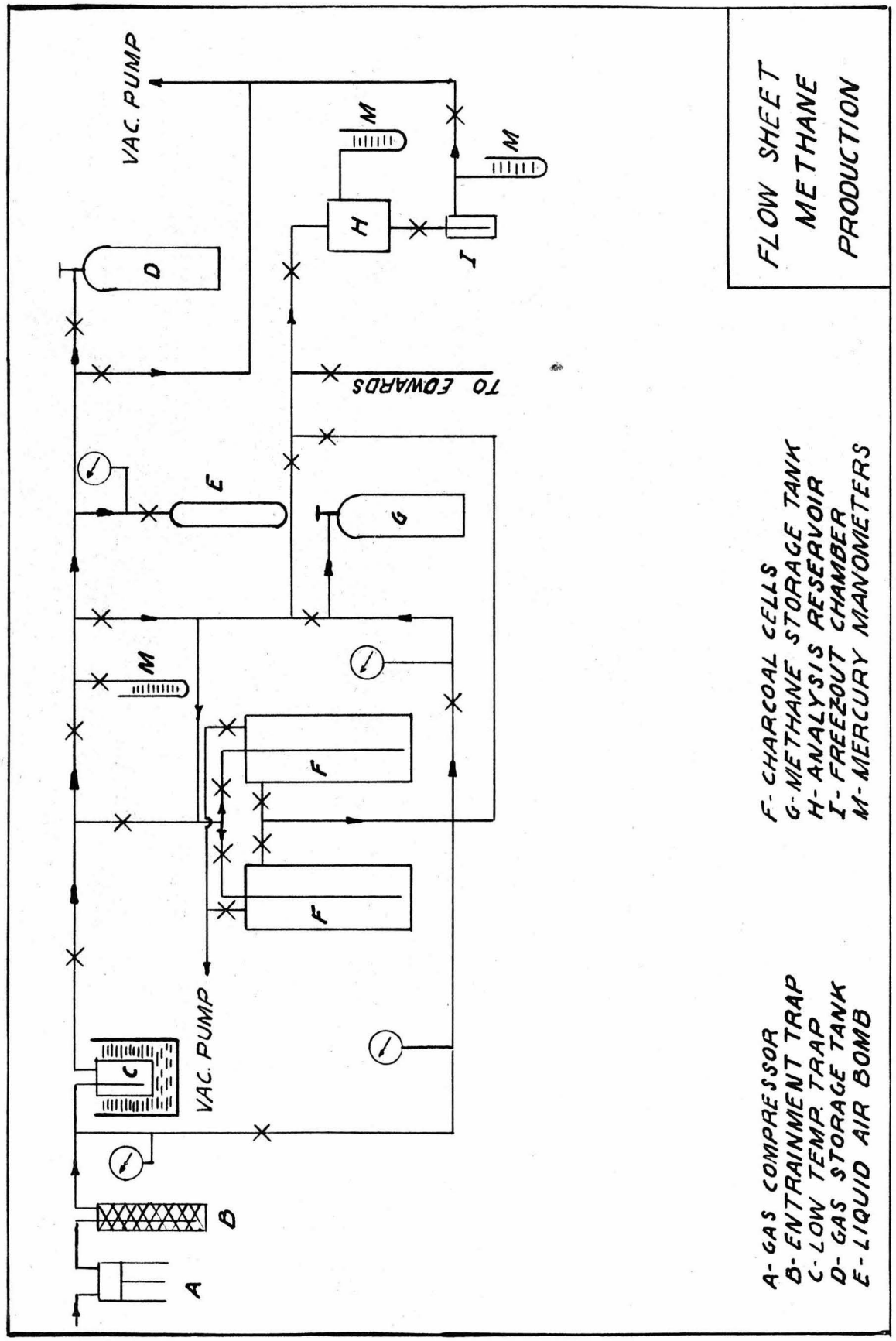

FLOW SHEET
METHANE
PRODUCTION
VAC. PUMP
VAC. PUMP
TO TOWARDS
A
B
C
D
E
F
F
G
H
I
M
M
M
A- GAS COMPRESSOR
B- ENTRAINMENT TRAP
C- LOW TEMP. TRAP
D- GAS STORAGE TANK
E- LIQUID AIR BOMB
F- CHARCOAL CELLS
G- METHANE STORAGE TANK
H- ANALYSIS RESERVOIR
I- FREEZOUT CHAMBER
M- MERCURY MANOMETERS

FIG. 3

from the compressor were removed, and into a steel bomb immersed in a bath of alcohol and solid carbon dioxide. The temperature and pressure here were such that the heavy hydrocarbons and mercaptans would condense out. The partly stripped gas was then passed into a steel bomb of about 900 c.c. volume (Fig.4), immersed in liquid air, where it was completely liquefied; gas being admitted until the bomb was nearly filled. The level of the liquid inside the bomb could be followed by observing the boiling of the liquid air on the outside of the bomb. The gas inlet valve was then closed, and while the bomb was still at liquid air temperature the line to the vacuum pump was opened, and most of the non-condensible gases were removed from the bomb. Vacuum was applied until the pressure in the bomb fell to about 8 or 10 cm. of mercury. The vacuum line was shut off, the liquid air jacket removed, and the bomb allowed to warm up, there-by causing an increase in pressure in the bomb. When the pressure reached 500 lbs. per sq. in., gas was throttled into the charcoal cell at such a rate as to maintain constant pressure in the bomb. The temperature of the bomb was measured by means of a thermocouple soldered to the bomb, and when this indicated that the temperature had risen to about -90 °C the line leading to the charcoal cell was closed. This prevented too much ethane from vaporizing and passing over into the cell. Liquid air was again applied to the bomb, and the cycle repeated until analysis of the outlet gas from the charcoal cell showed that the charcoal had become nearly saturated. In the charcoal cell, the gas passed by means of a small tube to the bottom of the cell, then up thru the charcoal to the top, where it was drawn off and placed in a storage tank.

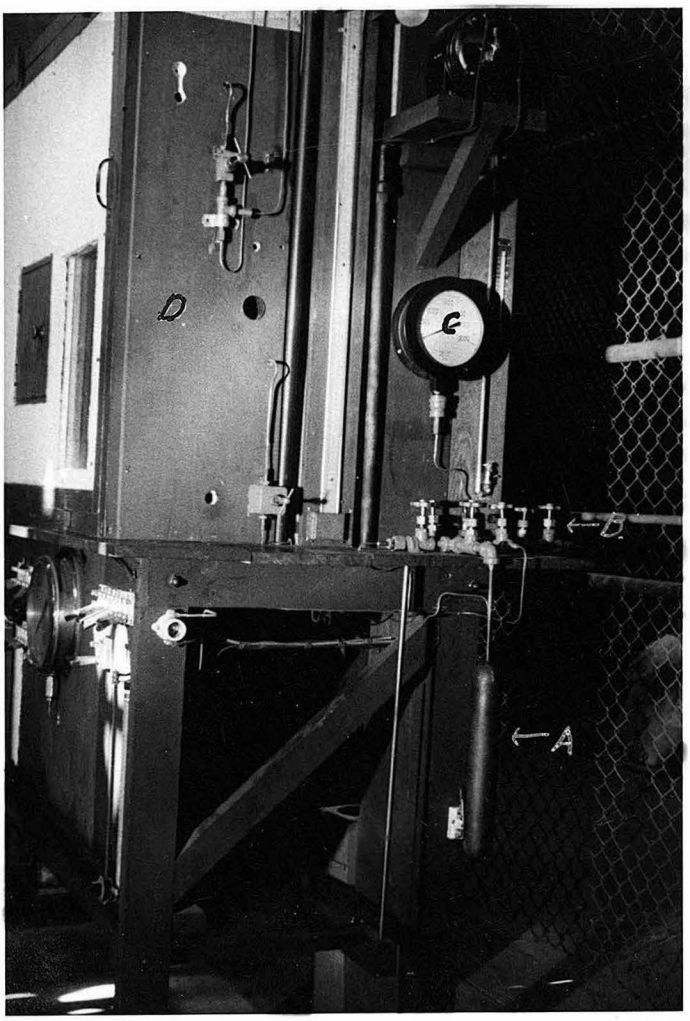


Fig. 4

A- Liquefying bomb

B- Control valves

C- Bourdon pressure gage

D- Air thermostat containing gas analysis apparatus

At the start the outlet valve of the charcoal cell was closed, and the pressure there-in increased as gas was admitted. When this pressure had built up to about 500 lbs. per sq. in. gas was bled from the top of the cell. The flow of gas into and out of the cell was so regulated that the cell pressure was maintained constant. The highest pressure attainable in the storage tank was that at which the charcoal cell was operated.

The average life of the charcoal in a cell was equivalent to an output of from 15 to 20 cu. ft. of gas measured at atmospheric pressure. Because the process was one of adsorption the end-point of charcoal usefulness was very sharp. The charcoal was re-activated by heating the cell to a temperature of about 220 °C for an hour or more, and at the same time maintaining low pressure by means of a vacuum pump. When at this temperature the pressure had been reduced to a few millimeters of mercury the heaters were turned off, and the line to the vacuum pump closed. City water was then circulated thru the cooling coil until the temperature of the cell had fallen nearly to room temperature. Water from the refrigeration tank was then circulated and when the temperature of the cell had been lowered to about 8 °C it was ready for use.

ANALYSIS OF METHANE PRODUCED

In order to follow the operation of the charcoal cell, analysis of the outlet gas was taken at intervals. The analysis was designed to give an indication of the per cent of hydrocarbons, heavier than methane, present. A sample of gas at about atmospheric pressure was stored in a reservoir(about 800 c.c. volume) to which was connected a mercury manometer. The

initial pressure of the gas in the reservoir was recorded. Gas was then pulled thru an evacuated copper coil immersed in liquid air at such a rate that the pressure did not rise above 8 mm.of mercury. At this pressure ethane and heavier hydrocarbons would condense out, the methane being removed by the vacuum pump. After about 90 c.c. of gas had been passed thru the coil, the valve was closed and the final pressure in the reservoir recorded. The vacuum pump was allowed to run for about a minute longer, in order to be sure that all of the methane had been removed. This was indicated by the pressure falling to zero. The valves at both ends of the freez-out coil being now closed, the liquid air jacket was removed, and the coil allowed to warm up to the temperature of the thermostat. In so doing the condensed hydrocarbons vaporized, causing the pressure to rise. The final pressure in the coil was read on the differential manometer, and by knowing the ratio of the volume of the reservoir to the volume of the coil, the per cent of ethane and higher hydrocarbons could be calculated. Analyses taken at different times during the cycle of operation are given in the appendix. The apparatus just described for making the gas analysis was placed in an air thermostat so that the temperature could be held constant. Gas densities were measured by means of the standard type of Edwards gas density balance.

DESIGN OF CHARCOAL CELLS

In order that the charcoal cells could be operated under high pressure it was necessary that they be made out of steel. A further requirement was that the cell be equipped with cooling and heating units for use during the adsorption and reactivation cycles. A vacuum connection to the cell was also necessary for

removal of gases during the period of charcoal re-activation. Taking these factors into consideration the final design of the cell was as follows: The chamber containing the charcoal was made from Shelby seamless steel tubing 3¼ in. outside diameter, 2¼ in. inside diameter, and 24 in. long. The tube was closed at the bottom by means of a screw plug which was welded around the edge after being tightened up. A flange was welded to the top of the tube for use in bolting on the head of the cell. Inside the cell a small steel tube, extending to the bottom of the cell, was welded to the gas inlet port. When completed, this high pressure cylinder was placed inside of a thin walled steel tube having about an inch larger diameter. A cooling coil made of 3/16 in. copper tubing was placed around the inner cylinder, and molten lead poured in until the annular space between the cell and outer tube was completely filled. The lead on solidifying served two purposes. First it supplied a complete metal path between the cell and the cooling and heating elements, there-by greatly increasing the heat conductivity. Secondly it held the cell and coil firmly in place within the enclosing metal shell. The electric heater was wound on the outside of the metal shell, and was insulated from it by means of asbestos paper and insolute cement. A thermometer well was placed in the cell head for use in taking temperatures. Gas lines were connected to the cell by means of standard fittings. The head of the cell was bolted on in order that it could be removed when desired. Cold water for the cooling coil was circulated, by means of a motor-driven pump, from a storage tank equipped with an electric refrigeration unit, thru the coil and back to the tank. The cooling coil was also connected to the tap water line so that city water could be used during the

preliminary cooling period, and to the compressed air line so that the coil could be blown free of water during the heating periods. The two cells were so arranged that when one was being used for methane production, the other could be heated and re-activated. The charcoal cells with their necessary vacuum, gas, and water connections are shown in Fig. 5.

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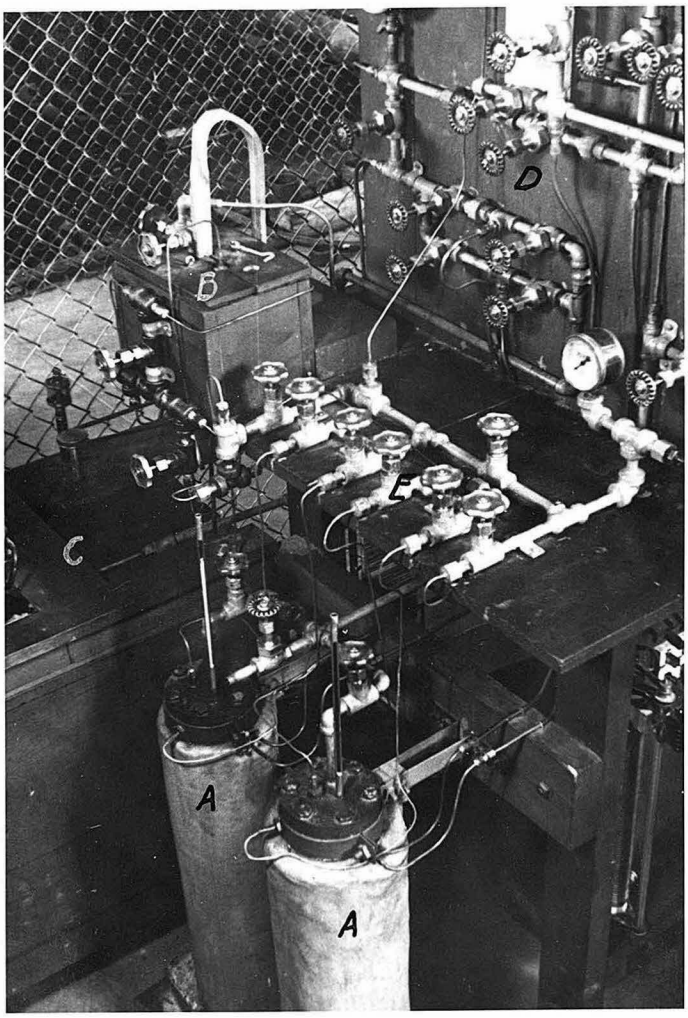

Fig. 5

A- Charcoal cells

B- Low temperature condensation trap

C- Tank containing refrigeration unit for cooling water

D- Control valves on air and water lines to charcoal cells

E- Metric valves for regulating flow of gas into and out of charcoal cells

APPENDIX

Solubilities are expressed in terms of cubic feet of gas, measured at 60°F. and at a pressure of 14.73 lbs. per sq. in., per barrel of 42 gal. of original oil.

The pressures given are gage pressures; but, since air was not removed from the apparatus, they are the partial pressures of the gas being forced into the apparatus.

With the exception of a few specially designed needle valves, Metric valves were used on all the high pressure equipment.

The Santa Fe Springs gas used for these experiments consisted approximately of 87% methane, 8% ethane, and 5% propane.

The city gas analysis was as follows: 83.3% methane, 15.8% ethane and higher hydrocarbons, and 0.9% nitrogen.

The analyses given below give some idea of the operation of the charcoal cells. The analysis figure gives only the per cent of ethane and heavier hydrocarbons present with the methane. One cycle as used below corresponds to one filling of the bomb immersed in liquid air and the passage of this amount of gas thru the charcoal cell.

Gas sample from cell at end of 1st cycle	0.022%
Gas sample from cell at end of 2nd cycle	0.031%
Gas sample from cell at end of 3rd cycle	0.17 %
Gas sample from bomb at end of vaporization period	2.94%
Gas sample from bomb after it had been allowed to warm up to 0°C. the pressure being kept at 400 lbs. per sq. in. by throttling out gas	18.7%
Gas sample from methane storage tank	0.13%